2

THE EFFECT OF CHAIN TRANSFER ON THE DISTRIBUTION OF MOLECULAR WEIGHTS IN HIGH POLYMERS. PART II. TERMINATION BY DISPROPORTIONATION

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ABSTRACT. An equation for distribution of molecular weights taking into account chain transfer with monomer, solvent and catalyst has been derived under the assumption that the chain termination is exclusively by disproportionation From this equation values of P_n, P_w, etc., have been derived and a number of relations deduced. All these equations are compared with similar equations derived previously assuming chain termination by combination of two growing radicals.

INTRODUCTION

In the previous paper of this series (Palit and Majumdar, 1954) we discussed the case where the termination takes place exclusively by coupling of two free radicals as is generally believed to be the case. However, as the possibility of termination by disproportionation cannot be completely ruled out we have considered in the present paper this latter mode of termination only, and have compared our previous findings with the present results.

DERIVATION OF THE DISTRIBUTION EQUATION

Let us consider the following kinetic scheme wherein we have used the same notations and abbreviations as in our earlier paper.

Initiation	$I+M \rightarrow X_1$		k_i
Propagation	$X_r+M \rightarrow X_{r+1}$		k_p
Transfer (monomer) ...	$X_r+M \rightarrow P_r+X_1$		k_M
Transfer (solvent) ...	$X_r+S \rightarrow P_r+S^*$		k_S
	$S^*+M \rightarrow S+X_1$		k_{S_1}
	$S^*+M \rightarrow SX_1$		k_{S_2}
Transfer (catalyst) ...	$X_r+I \rightarrow P_r+I^*$		k_I
	$I^*+M \rightarrow I+X_1$		k_{I_1}
	$I^*+M \rightarrow IX_1$		k_{I_2}
Termination (disproportionation)	$X_r+X_s \rightarrow P_r+P_s$		k_t

Also, let $q = C_M + C_S S/M + C_I I/M + t\sqrt{I/M}$; and $t = \frac{\sqrt{k_i k_t}}{k_p}$

From the above scheme with the usual steady state assumption and using a method exactly similar to that used in our previous paper (vide Appendix) the following distribution equation is obtained.

$$\omega_r = r \times \left(-\frac{dP_r}{dM}\right) = \frac{q^2 r}{(1+q)^2(1+\epsilon_j)} \simeq \frac{q^2 r}{(1+q)^r} \qquad \ldots \quad (1)$$

where ω_r is the weight fraction of the r-mers. Making resonable approximations (vide Appendix) we finally obtain

$$\omega_r = q^2 r e^{-qr} \qquad \ldots \quad (2)$$

This equation is very similar to that obtained by Bawn (1948) without considering any kind of transfer.

Equation (2) is a differential equation and so gives the instantaneous distribution at a given value of S/M and I/M and so it should be applied to experimental data at small yields.

It should be noted that the distribution equation is a function of q only and does not involve any other quantity explicitly and hence the effect of a change of any factor is simply obtained by noting the effect of a change of q only. Thus, we need not consider individually the effect of the single factors, viz., S, I, C_M, C_S, C_I and $t = \frac{(k_i k_t)^{1/2}}{k_p}$, but we need only study the distribution curves within the usual experimental range of variation of $q = C_M + C_S S/M + C_I I/M + t\sqrt{I/M}$, which has been done in the next section.

THE SHAPE OF THE THEORETICAL DISTRIBUTION CURVE

In figure 1 we have drawn a set of curves with values of q from 1×10^{-4} to 5×10^{-4}. It may be mentiond that $q = 1.24 \times 10^{-4}$ would represent polymerization of styrene at 60°C and so curves with $q = 2 \times 10^{-4}$ and higher would represent its gradual change either by addition of a solvent or a catalyst, or by raising temperature. The shape is quite similar to the theoretical curves for termination by combination but the present curves are a little steeper. To have a comparative idea we have drawn in figure 2 two curves corresponding to the same polymerization constants, the mechanism of termination being by coupling and disproportionation respectively. It is found that on changing from coupling to disproportionation, the major change in the distribution curve is that the height of the maximum is somewhat raised and the value of the most probable D. P. is somewhat lowered. This is more easily seen from the expressions of these quantities given in a table later.

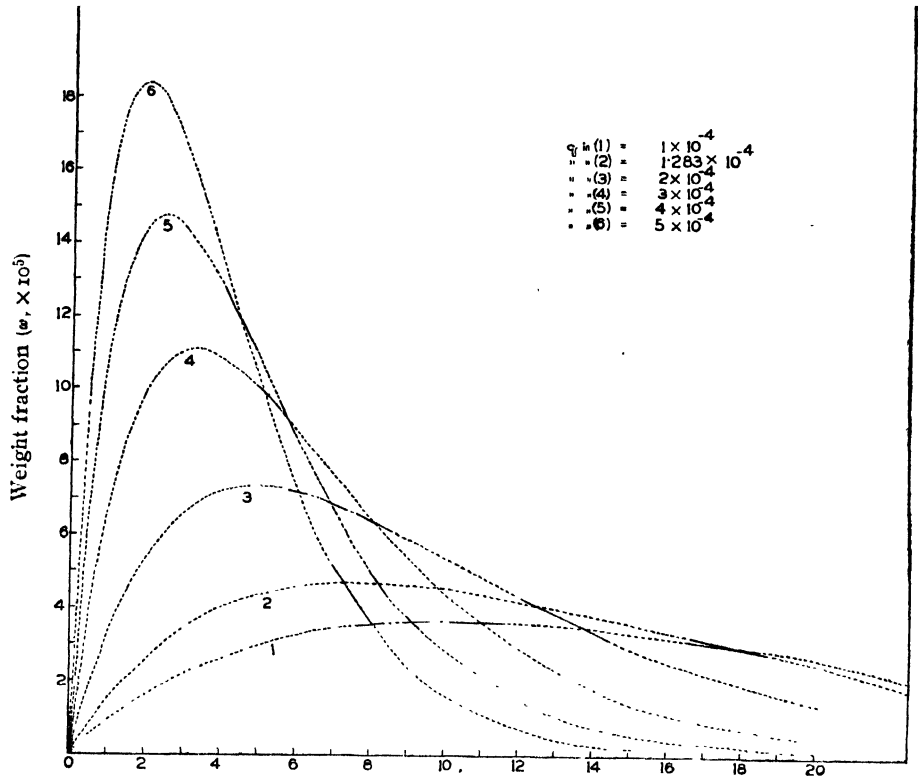

FIG. 1. Degree of polymerization ($r \times 10^{-3}$)

The main difference between the present distribution function for disproportionation and that for combination can be brought forth to a sharp relief by rewriting the latter as shown below.

Coupling :
$$\omega_r = q^2 r e^{-qr}\left(1 - \frac{t}{q}\sqrt{\frac{\bar{I}}{M}}\left\{1 - \frac{q(r-1)}{2}\right\}\right)$$
$$\simeq q^2 r e^{-qr}\left(1 - t\sqrt{\frac{\bar{I}}{M}}\left\{\frac{1}{q} - \frac{r}{2}\right\}\right)$$

Disproportionation : $\omega_r = q^2 r e^{-qr}$

It can be clearly seen from the above equations that for the same set of values of the constants ω_r for combination contains an additional factor to ω_r for disproportionation, this factor being

$$1 - t\sqrt{\frac{\bar{I}}{M}}\left\{\frac{1}{q} - \frac{r}{2}\right\}$$

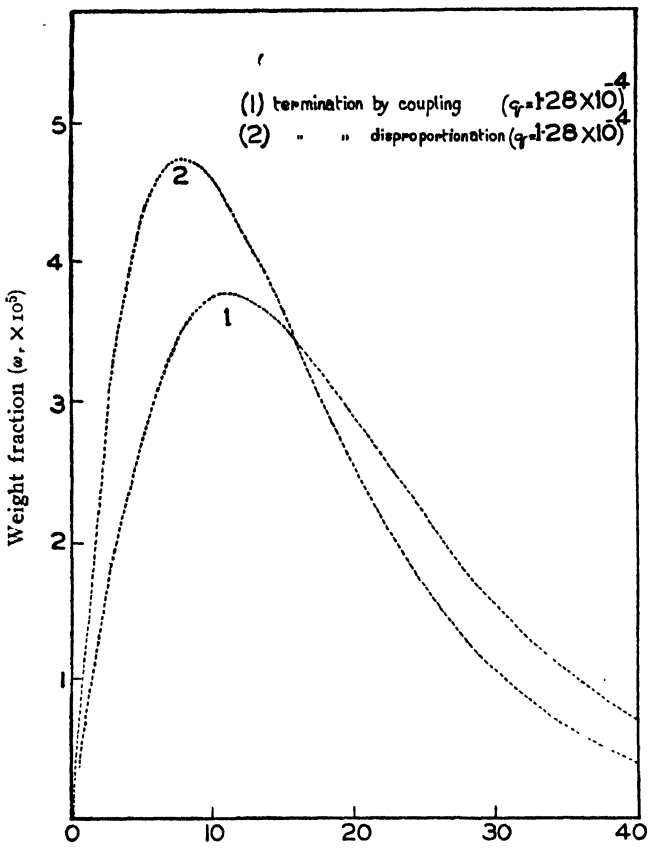

FIG. 2. Degree of polymerization ($r \times 10^{-3}$)

which is equal to, less than or greater than unity according as

$$r=\frac{2}{q},\ <\frac{2}{q} \text{ or } >\frac{2}{q}$$

respectively. This is clearly shown graphically in figure 2 where it would be seen that the combination line runs lower than the disproportionation line up to $2/q$, from beyond which the reverse is the case.

INTERQUARTILE DISTANCE AND STEEPNESS OF DISTRIBUTION

The interquartile range Δr is given by a very simple relation (vide Appendix),

$$\Delta r=r_2-r_1=\frac{1.7}{q}=1.7\overline{P_n} \qquad \ldots (3)$$

Thus Δr depends only on q and is inversely proportional to q, so that interquartile range decreases with an increase in q and therefore, with an increase of C_S or S/M or I/M or t. Therefore, $1/\Delta r$ bears an exact linear relationship with q and hence, with C_S(S/M) at any temperature (i. e. for

any value of t with a slope of 0.58. In the case of coupling such relation between the reciprocal of interquartile range and $C_S'S/M$) is only approximately linear at constant temperature with a slope varying from 0.48 to 0.58 i. e., near about half.

MOST PROBABLE DISTRIBUTION

The D. P., r_0, the proportion of which is maximum in a given sample, is calculated in the usual manner (vide Appendix) and is found to be exactly equal to $1/q$ and hence to $\bar{P}_n$, the number average D. P. In other words correlation of r_0 and $\bar{P}_n$ does not depend upon any rate constant or proportion of solvent andi s independant of temperature. This is not the case with distribution for coupling, where the correlation of r_0 and $\bar{P}_n$ does depend on temperature (i. e., t), although r_0 is very nearly equal to $\bar{P}_n$ under all conditions (also at ny temp.) within a maximum positive deviation of 8% $\left(i.e.\ 1 \leq \frac{r_0}{\bar{P}_n} \leq 1.08\right)$.

WEIGHT AVERAGE AND NUMBER AVERAGE D. P.

By employing standard methods (vide Appendix) we obtain the following relation between the weight average D. P., $\bar{P}_w$ and number average D. P., $\bar{P}_n$

$$\bar{P}_n = \frac{1}{2}\bar{P}_w = \frac{1}{q} \qquad \ldots \quad (4)$$

From kinetic considerations, also we get

$$\frac{1}{\bar{P}_n} = \frac{\text{rate of cessation of chain}}{\text{rate of propagation}} = C_M + C_S\frac{S}{M} + C_I\frac{I}{M} + t\sqrt{\frac{I}{M}} = q$$

which is quite in agreement with that obained by direct integration of the distribution equation and so the identity of our distribution equation with the kinetic chain length equation is also completely established in case of chain termination by disproportionation.

Equation (4) shows that the ratio $\bar{P}_w/\bar{P}_n$ is uniquely given by $\bar{P}_w/\bar{P}_n = 2$ and neither depends upon any rate constant nor on temperature nor on the proportion of any solvent, unlike in the case of chain terminations by coupling, in which case we have $1.5 \leq \bar{P}_w/\bar{P}_n \leq 2$. From most experimental results the ratio is found to be near about 2, but if some experimental condition is obtained with $S=0$ and $t => C_M$, $\bar{P}_w/\bar{P}_n$ will be very near to 1.5, in which case one can decisively conclude the absence of termination by disproportionation.

MAXIMUM WEIGHT FRACTION

It has been shown in the Appendix that the maximum weight fraction ω_r, corresponding to the most probable D. P. enters into a simple relation with q in either termination by disproportionation or by coupling.

Thus, in case of disproportionation

$$\omega_{r_0} = 0.37q = 0.37/\bar{P}_n = 0.37/r_0$$

or $$\omega_{r_0} - 0.37t\sqrt{I/M} = 0.37(C_M + C_S S/M + C_I I/M)$$

and in case of combination $\omega_{r_0} = 0.37q - 0.1t\sqrt{I/M} = 0.37/\bar{P}_n + 0.085t\sqrt{I/M}$

or $$\omega_{r_0} - 0.27t\sqrt{I/M} = 0.37(C_M + C_S S/M + C_I I/M)$$

Thus, the expressions for the maximum weight fraction for both the termination processes are similar with the only difference that ω_{r_0} in the case of combination is less than that for disproportionation by an amount $0.1t\sqrt{I/M}$ which can be, at the most, 27 per cent when $t\sqrt{I/M}$ is equal of q that is when $C_M \to 0$ and uncatalysed bulk polymerization is considered.

It is also seen that the plot of ω_{r_0} minus $0.37t\sqrt{I/M}$ in case of disproportionation and minus $0.27t\sqrt{I/M}$ in case of combination against $C_S S/M$ is exactly linear with a slope of 0.37 for same monomer and catalyst (initiation) and at any temperature. These result may be experimentally tested.

COMPARISON OF COMBINATION AND DISPROPORTIONATION

In order to bring into focus the distinction between the two cases the main features are summarised in the table below.

	Disproportionation	Combination
Distribution equation	$\omega_r = q^2 r e^{-qr}$	$\omega_r = qr(a+b)e^{-qr} = q^2 r e^{-qr}\left[1 - t\sqrt{I/M}\left(\frac{1}{q} - \frac{r-1}{1}\right)\right]$
Maximum weight fraction	$\omega_{r_0} = \frac{q}{e} = 0.37q = 0.37/P_n$	$w_{r_0} = t\sqrt{I/M}(1+\sqrt{1+x^2})e^{-(1-x+\sqrt{1+x^2})} \simeq 0.37q - 0.1t\sqrt{I/M} = 0.37/P_n + 0.085t\sqrt{I/M}$
Most probable D. P. r_0	$r_0 = 1/q$	$r_0 = 2/q - \frac{1}{t\sqrt{I/M}} + \sqrt{q^2 - \frac{2}{q}\cdot\frac{1}{t\sqrt{I/M}} + \frac{1}{t^2 I/M}}$
Number average $\bar{P}_n$	$\bar{P}_n = 1/q$	$\bar{P}_n = 1/(q - \frac{1}{2}t\sqrt{I/M})$
Weight average D. P. $\bar{P}_w$	$\bar{P}_w = 2/q$	$\bar{P}_w = \frac{2}{q} + \frac{t\sqrt{I/M}}{q^2}$
Relation between $\bar{P}_n$ and $\bar{P}_w$	$\bar{P}_n = r_0$	$P_n \leq r_0 \leq 1.08P_n$
Relation between $\bar{P}_n$ and r_0	$\bar{P}_w/\bar{P}_n = 2$	$1.5 \leq \frac{\bar{P}_w}{\bar{P}_n} \leq 2.0$
Variation in interquartile distances	$\frac{1}{\Delta r} = \frac{q}{1.7} = \frac{1}{1.7\bar{P}_n}$	$\frac{1}{\Delta r} \simeq \frac{q}{2} = \frac{1}{2P_n} + \frac{1}{4}t\sqrt{I/M}$

EXPERIMENTAL TEST

All equations deduced so far are subject to experimental test and experimental work is in progress with a view to obtaining data not only to test these equations quantitatively but also to throw light on the nature of the terminating process.

APPENDIX

Derivation of the Distribution Function :

For the given kinetic scheme we have for steady state

$$\frac{dX_r}{dt} = k_p X_{r-1} M - k_p X_r M - k_M X_r M - k_S X_r S - k_I X_r I - k_t X_r C^* = 0 \qquad (1)$$

$$\frac{dX_1}{dt} = k_i IM - k_p X_1 M + k_M C^* M - k_M X_1 M - k_S X_1 S + (k_{S_1} + k_{S_2}) S^* M - k_1 X_1 J + (k_{I_1} + k_{I_2}) I^* M - k_t X_1 C^* = 0 \qquad (2)$$

$$\frac{dS^*}{dt} = k_S C^* S - (k_{S_1} + k_{S_2}) S^* M = 0 \qquad (3)$$

and $$\frac{dI^*}{dt} = k_I C^* I - (k_{I_1} + k_{I_2}) I^* M = 0 \qquad (4)$$

where C^* = total concentration of radicals $= \sum_{r=1}^{\infty} X_r$ (5)

The above equations and the further steps upto the derivation of the expression for X_r are exactly similar to those in Appendix I of our previous paper (Palit and Majumdar, 1954). Hence the following results are simply quoted without going again into the details of those steps.

$$C^* = \left(\frac{k_i}{k_t} IM \right)^{\frac{1}{2}} \qquad (6)$$

$$X_1 = \frac{q(k_i/k_t IM)^{\frac{1}{2}}}{(1+q)} \qquad (7)$$

$$X_r = \frac{q(k_i/k_t IM)^{\frac{1}{2}}}{(1+q)^r} \qquad (8)$$

where $$q = C_M + C_S \frac{S}{M} + C_I \frac{I}{M} + t\sqrt{\frac{I}{M}} \qquad (9)$$

and $$C_X = k_X / k_p$$

Now from the kinetic scheme for the termination by disproportionation we have,

$\frac{dP_r}{dt} = k_M X_r M + k_S X_r S + k_I X_r I + k_t X_r C^*$, which by (8) and (9) reduces to

$$\frac{dP_r}{dt} = k_p M q X_r = \frac{k_p M q^2 \{(k_i/k_t) IM\}^{\frac{1}{2}}}{(1+q)^r} \quad \ldots \quad (10)$$

Also $$-\frac{dM}{dt} = k_p C^* M + k_M C^* M - k_M X_1 M + k_i IM + (k_{S_1} + k_{\bar{S}_2}) S^* M$$
$$- k_S X_1 S + (k_{I_1} + k_{I_2}) J^* M - k_1 X_1 I - k_t X_1 C^*$$
$$= k_p C^* M + k_M C^* M - k_M X_1 M + k_i IM + k_S C^* S$$
$$- k_S X_1 S + k_I C^* I - k_I X_1 I - k_t X_1 C^*, \text{ by (3) and (4)}$$

Substituting the values of C^* and X_1 from (6) and (7) this reduces after simplication to

$$-\frac{dM}{dt} = k_p M (k_i/k_t IM)^{\frac{1}{2}} \left(1 + \frac{q}{1+q}\right) = k_p M (k_i/k_t IM)^{\frac{1}{2}} (1+\epsilon) \quad \ldots \quad (11)$$

where $$\epsilon = \frac{q}{1+q} << 1$$

From (10) and (11) we thus have

$$-\frac{dP_r}{dM} = \frac{dP_r/dt}{-dM/dt} = \frac{q^2}{(1+q)^r (1+\epsilon)} = \frac{q^2}{(1+q)^r} \quad \ldots \quad (12)$$

as $$\epsilon << 1$$

This is exactly the same as the expression found by Bawn, but with

$$k_M = k_S = k_{S_1} = k_{\bar{S}_2} = k_c = k_{I_1} = k_{I_2} = k_1 = 0$$

The instantaneous distribution function of the molecular weights is then given by

$$\omega_r = r \times \left(-\frac{dP_r}{dM}\right) = \frac{rq^2}{(1+q)^r (1+\epsilon)}$$

or neglecting ϵ as compared to unity

$$\omega_r = \frac{qr}{(1+q)^r} \quad q^2 r e^{-qr} \quad (13)$$

by putting $(1+q)^r = e^x$, whence $x = r \ln(1+q) \simeq rq$ as $q << 1$

INTERQUARTILE DISTANCE OF THE DISTRIBUTION FUNCTION

If r_1 and r_2 be the lower and upper quartiles respectively we shall have

$$\frac{1}{4} = \int_0^{r_1} \omega_r dr = \int_{r_2}^{\infty} \omega_r dr$$

Substituting for ω_r from (13) we have after integrating by parts

$$\frac{1}{4} = \int_0^{r_1} q^2 r e^{-qr} dr = q^2 \left\{ \left[-\frac{re^{-qr}}{q} \right]_0^{r_1} + \frac{1}{q} \left[-\frac{e^{-qr}}{q} \right]_0^{r_1} \right\} = -qr_1 e^{-qr_1} - e^{-qr_1} + 1$$

or $$\frac{3}{4} e^{x_1} = 1 + x_1 \quad \ldots \quad (14)$$

where $x_1 = qr_1$

Similarly, $\frac{1}{4}e^{x_1} = 1 + x_2$ ... (15)

where, $x_2 = qr_2$

The equations in (14) and (15) can be solved graphically exactly in the same way as the corresponding equations of Appendix II of our previous paper (Palit and Majundar, 1954), taking as if p is zero. The solution will yield

$$\Delta x = x_2 - x_1 = 1.7, \text{ so that}$$

$$\Delta r = r_2 - r_1 = \frac{x_2 - x_1}{q} = \frac{1.7}{q} \quad \ldots (16)$$

which is the interquartile distance.

WEIGHT AVERAGE D. P. ($\bar{P}_w$)

From definition it follows

$$P_w = \frac{\Sigma r\omega_r}{\Sigma\omega_r} = \Sigma r\omega_r, \text{ because } \Sigma\omega_r = \int_0^\infty \omega_r dr = \int_0^\infty q^2 re^{-qr}dr = 1$$

$$\simeq \int_0^\infty r\omega_r d_r = \int_0^\infty r^2q^2e^{-qr}dr = \frac{2}{q} \quad \ldots (17)$$

NUMBER AVERAGE D. P. ($\bar{P}_n$)

Similarly the number average D. P. is given by

$$P_n = \frac{\Sigma rP_r}{\Sigma P_r} = \frac{\Sigma\omega_r}{\Sigma q^2 e^{-qr}} \simeq \frac{1}{q^2\int_0^\infty e^{-qr}dr} = \frac{1}{q} \quad \ldots (18)$$

Evidently $\bar{P}_w/\bar{P}_n = 2$

MOST PROBABLE D. P. (r_0)

The D. P. corresponding to the maximum proportion (weight fraction) of the distribution is obtained by maximising ω_r with respect to r. Thus r_0 is the solution of

$$\frac{\partial\omega_r}{\partial r} = \frac{\partial}{\partial r}[q^2re^{-qr}] = 0$$

or $-qr_0e^{-qr} + e^{-qr} = 0$, giving $r_0 = \frac{1}{q}$ ... (19)

It can be easily seen from (17), (18) and (19) that

$$r_0 = \bar{P}_n = \tfrac{1}{2}\bar{P}_w = \frac{1}{q} \quad \ldots (20)$$

MAXIMUM WEIGHT FRACTION (w_{r_0})

Expression for the maximum weight fraction ω_{r_0} will be obtained by putting the value of r_0 in distribution equation. Thus for disproportionation we have by virtue of relation (19)

$$\omega_{r_0} = q^2 r_0 e^{-qr_0} = \frac{q}{e} = 0.37(C_M + C_S S/M + C_I I/M + t\sqrt{I/M}) \quad \ldots (21)$$

Similar expression for ω_{r_0} for termination by coupling can also be derived in the following way. This was, however, not discussed in our previous paper. For the termination by coupling we get

$$\omega_{r_0} = qr_0(\tfrac{1}{2}qt\sqrt{I/M}r_0 + q - t\sqrt{I/M})e^{-qr_0} \quad \ldots (22)$$

Since r_0 in such case is

$$r_0 = \frac{2}{q} - \frac{1}{t\sqrt{1/M}} + \sqrt{\frac{2}{q^2} - \frac{2}{qt\sqrt{I/M}} + \frac{1}{t^2 I/M}} \quad \ldots (23)$$

then on substitution of (23) in (22) and applying the transformation

$$x = \frac{C_M + C_S S/M + C_I I/M}{t\sqrt{I/M}} = \frac{q - t\sqrt{I/M}}{t\sqrt{I/M}} \quad \ldots (24)$$

the expression in (22) for the maximum weight fraction for combination reduces to

$$\frac{\omega_{r_0}}{t\sqrt{I/M}} = (1 + \sqrt{1+x^2})e^{-(1-x+\sqrt{1+x})} \quad \ldots (25)$$

From this it is easily seen that $\frac{\omega_{r_0}}{t\sqrt{I/M}}$ is represented by an universal equation independent of temperature, monomer, solvent or any catalyst initiator or their proportion in a particular reaction. Equation (25) although looks complicated represents a straight line upto the range even beyond the value of $x = 400$ a value which we shall never have in practice. The slope and intercept of the straight line found statistically (by fitting a a straight line to a number of points obtained from (25) and then applying usual chi-square test) are respectively 0.37 and 0.27, so that for combination we can write

$$\frac{\omega_{r_0}}{t\sqrt{I/M}} = 0.27 + 0.37x$$

Substituting in this the value of x from (24) we get

$$= 0.27 + 0.37\left(\frac{q - t\sqrt{I/M}}{t\sqrt{I/M}}\right)$$

or $$\omega_{r_0} = 0.37q - 0.1t\sqrt{I/M} = 0.37(C_M + C_S S/M + C_I I/M) + 0.27t\sqrt{I/M} \quad \ldots (26)$$

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